Chapter 6 Halohydrocarbon

通式:R-X



Classification:

卤代烷

按烃基不同

卤代烯烃

卤代芳烃 Ar-X

·芳香卤代烃Ar(CH₂)_nX

按卤素数目不同:

国」が下

多卤代烃

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RCH₂-X 伯卤代烷

仲卤代烷 R₂CH-X

R₃C-X 叔卤代烷

乙烯型卤代烃 RCH=CHX

卤代烯烃 ≺烯丙基型卤代烃 RCH=CHCH₂X

-孤立型卤代烃 RCH=CH(CH₂)_nX



二、 Nomenclature:

1、简单的卤代烃:

"卤某烃"或"某烃基卤"

CH₃CH₂Br (CH₃)₃CCI Ph-CH₂CI

溴乙烷

叔丁基氯

苄基氯



2、复杂的卤代烃:(系统命名法)

特点: 卤素作为取代基

CH₃Br C₆H₅ CH₃CHCHCHCH₂CH₃

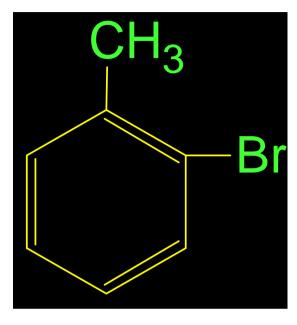
2-甲基-4-苯基-3-溴己烷

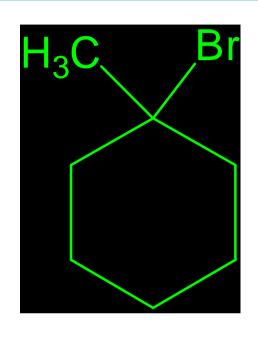
$$CH_3$$

 $CH_3CH_2C=C-C=C-CH_3$
 CI

5-甲基-4-氯-4-庚烯-2-炔







2-溴甲苯

(邻-溴甲苯)

1-甲基-1-溴环己烷



\equiv Chemical Properties:

 δ^+ δ^- R-CH₂-CH₂-X

亲核取代反应

(Nucleophilic Substitution Reaction)

消除反应

(Elimination Reaction)



1、亲核取代反应

反应通式:

R-X + Nu:- $R-Nu + X^{-}$

(底物)(亲核试剂) (产物)(离去基团)

常见的亲核试剂:

 OH^- , CN^- , ONO_2^- , NH_3



①卤素被羟基取代

R-X + NaOH
$$\longrightarrow$$
 R-OH + NaX (水溶液) (醇)

可用卤代烃制备醇





②卤素被氰基取代

R-X + NaCN → R-CN+ NaX (醇溶液) (腈)

此反应可增长碳链

 $\triangle \mid H_2O/H^+$

R-COOH

(羧酸)





③卤素被氨基取代

$$R-X + NH_3 \longrightarrow R-NH_2 + HX$$
 (胺)

RNH₃+X⁻ (铵盐)



④卤素被硝酸根负离子取代

 $R-X + AgONO_2$ \longrightarrow $R-ONO_2 + AgX$ (醇溶液) (硝酸酯)

AgCl(白色) AgBr(浅黄色) Agl(黄色)

此反应可用于物质的鉴别



举例:

NaCN(醇) → CH₃CH₂CH₂CN

CH₃CH₂CH₂Br

 $\frac{\mathsf{AgNO}_3(\mathbf{P})}{\wedge} \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}_2\mathsf{ONO}_2$

NaOH (水) CH₃CH₂CH₂OH

2、消除反应

(卤原子与β-H同时离去,形成烯烃.

此反应叫消除反应,也叫β-消除反应)

消除反应的反应条件:

碱性、醇溶液、加热



CH₃CH-CHCH₂ H X H KOH/乙醇

CH₃CH=CHCH₃
(81%)

 $CH_3CH_2CH=CH_2$ (19%)

结论:

(Sayteff)取向规则:

发生消除反应时,一般易生成双键 碳原子上所连烃基最多的烯烃。

实质: 生成最稳定的烯烃。



举例:

$$CH_3$$
 $-CH$
 $-CH$
 $-CH$
 $-CH$



(CH₃)₂CH-C(CH₃)₂ CI

 $(CH_3)_2C=C(CH_3)_2$

 $\begin{array}{c} \mathsf{CH}_3\\ \mathsf{H}_2\mathsf{C} \\ \mathsf{CH} \\ \mathsf{CH}_2\mathsf{CH} \\ \mathsf{CH}_2\mathsf{CH}_3\\ \mathsf{Br} \end{array}$

NaOH (醇)

 CH_3 $H_2C=CH-CH=CH-CH-CH_2$ CH_3



比较下列化合物的消除反应的活性:

CH₃CH₂CH₂CH₂CH₂Br

CH₃CH₂CH₂CH=CH₂

CH₃CH₂CHCH₃

CH₃CH₂CH=CHCH₃

Br CH₂=CHCH₂CHCH₃

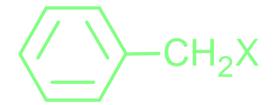
CH₂=CHCH=CHCH₃



四、卤代不饱和烃的亲核取代反应活性:

烯丙基型 ~ 苄基型

RCH=CHCH₂X



孤立型 RCH=CH(CH₂)_nX

乙烯型 ~ 卤代苯

RCH=CHX



大

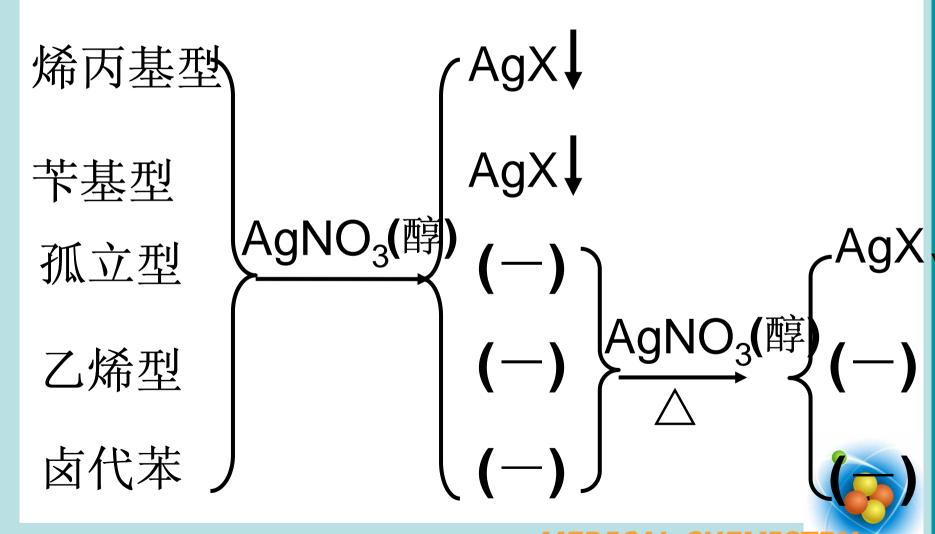
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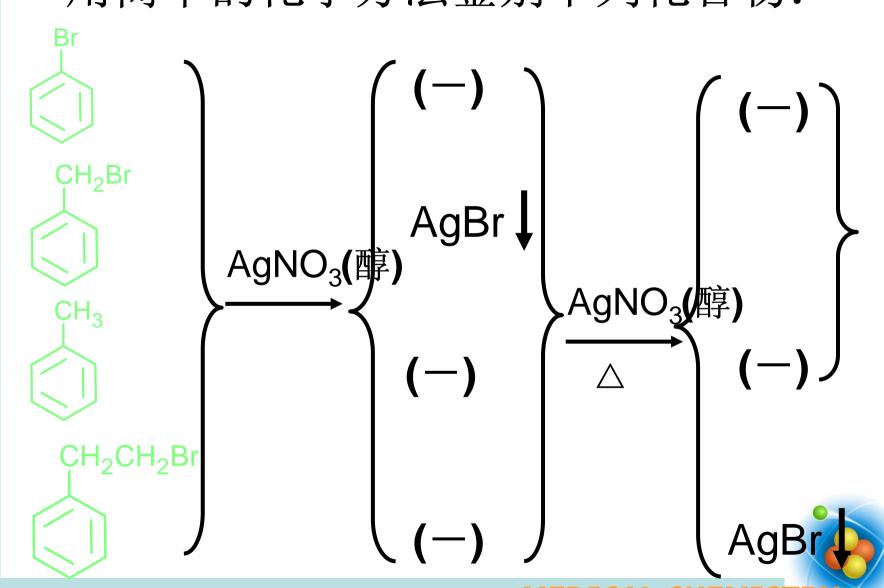
举例:



不同卤代烃与AgNO₃(醇)的反应

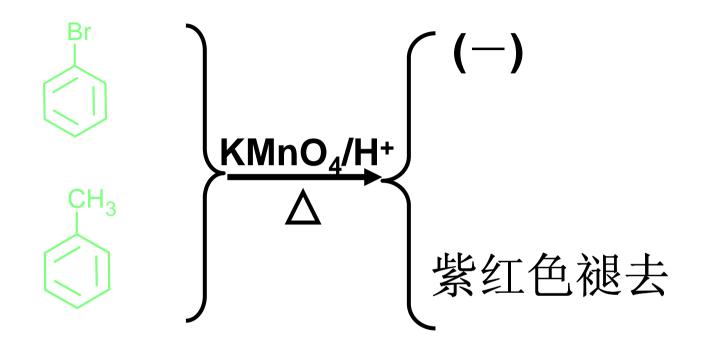


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The main chemical property of halohydrocarbon is nucleophilic substitution reaction. Because of the polarity of carbon-halogen bond in halohydrocarbon, the halogen atom of the bond leaves away from the molecule in the form of negative ion, while the nucleophilic reagent with rich electron replaces it.

The halogen that connects directly unsaturated carbons with halohydrocarbon shows very low activity nucleophilic substitution reaction. When it connects with a saturated carbon, its activity of reaction will increase. When it connects with benzyl group or allyl group, its activity of reaction increases greatly.



Under certain conditions, the nucleophilic reagent in the strong alkaline solvent attacks the β hydrogen instead of the α carbon so as to result in the elimination reaction of halohydrocarbon.





Exercises: (Page 117)

1, (2) (8)

2, (2) (4) (6)

4, (1) (2) (3) (5) (8)

8, (2) (3) (4)

11、(2)

12、